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From H. Author

ANALYSIS

OF THE

BATH WATER.

BY

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1806.

ANALYSIS

BATH WATER

ST. JOHN'S CHURCH



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1881

THE experiments contained in the following Analysis were commenced during an occasional residence at Bath, and read before the Askesian Society. Several of the facts occurring during the investigation having excited the attention of some chemical friends, a few copies have been printed for their perusal.

29 Poultry,

June 1806.

ANALYSIS

OF THE

HOT SPRINGS AT BATH.

THE nature of the country round Bath, and other local circumstances, have been so fully described by those who have given chemical examinations of the waters of the hot springs at that place, that any further description appears unnecessary.

As to the cause of the heat of these springs, we have so few data from which to reason, that I shall not offer even a conjecture on the subject.

These waters have been frequently analysed. They have merited the attention they have received, not only from their early and extensive employment in the cure of diseases, but also on account of some peculiar changes to which they are subject. Of these the explanations have been so various as to show that they require still further examination.

Of the sensible properties exhibited by these waters the most remarkable is their high temperature, the degree of which varies considerably at their different sources. At the hot bath it is 117° ; at the king's bath 114° ; and at the cross bath 109° . This statement does not exactly agree with what has been usually given as their temperature. These results were obtained by pumping the water upon the bulb of a thermometer till the mercury ceased to rise. Their taste is metallic, but not strongly or disagreeably so; this has not been universally allowed: but if they are drunk hot, this impression is readily distinguishable.

Their specific gravity is 1.002 at each of the springs; and as the effects produced by chemical tests are also perfectly similar, they may be considered as derived from one source, the temperature varying by their more or less circuitous passage to the surface. For the purpose of analysis the water of the king's bath has been usually employed; and, although it does not appear to be a matter of much importance, I have followed the usual practice.

Before the experiments made upon the water are related, it will be necessary to state those employed to ascertain the properties of the gas, which rises in great quantity through the water in the king's bath.

This gas is perfectly free from smell.

A

Some of the gas was received into a jar. A lighted taper put into it was immediately extinguished.

B

Received into lime water, it caused an immediate precipitation.

3

C

Tincture of litmus suffered no change of colour by agitation with the gas.

D

The colour of dilute tincture of turmeric and infusion of galls was destroyed by it.

From these effects the gas appears to consist principally of nitrogen gas with a small portion of carbonic acid gas. To ascertain the quantity of each, and whether any oxygen gas was present, the following experiments were performed:

E

One hundred measures of the gas were strongly agitated with barytes water in a graduated tube. A considerable precipitate was deposited, and five measures were absorbed.

F

One measure of nitrous gas was added to an equal quantity of the gas in an eudiometer in the water apparatus. The mixed gases underwent no alteration of colour or diminution of volume.

G

One hundred measures of the gas which had been deprived of carbonic acid by barytes water were submitted to the action of solution of green muriate of iron impregnated with nitrous gas. No absorption took place.

This gas, therefore, consists of,

Carbonic acid gas	.	.	5
Nitrogen gas	.	.	95
			<hr/>
			100
			<hr/>

I now proceeded to try whether the water held either of these gases in solution.

H

Ten ounces of the water, which had been cooled in a well-closed bottle, were put into a vessel furnished with a bent tube; the water was boiled for about twenty minutes, and the gas evolved from the water and the air of the tube, except a quantity too small to be estimated, were received in a graduated jar over mercury. Solution of potash absorbed 3-4ths of an inch this gas, which was carbonic acid.

I

The unabsoved gas was transferred to the water apparatus, and tried in the usual way with nitrous gas. The mean result of comparative experiments upon it and atmospheric air showed that it was merely the air of the vessel, and that no nitrogen gas was held in solution by the water.

As ten ounces of the water gave $\cdot 75$ of an inch of carbonic acid, one quart would furnish $2\cdot 4$. This quantity is not quite exact, it being scarcely possible to obtain the whole of the carbonic acid by ebullition.

Effects of Atmospheric Air and Re-agents.

K

Some of the water, while hot, having been exposed in a vessel of broad surface to the atmosphere, afforded in a few hours a small quantity of a white precipitate; but water which had been cooled in a close vessel remained perfectly transparent after several weeks exposure to the air.

The re-agents added to the water while hot, and the effects produced by them were the following:

L

Acetate of lead,—a perfectly white precipitate.

M

Tincture of litmus,—no alteration of colour.

N

Tincture of turmeric,—no change indicating the presence of uncombined alkali; its colour immediately almost destroyed.

O

Lime-water,—a white precipitate.

P

Ammonia,—a white precipitate.

Q

Carbonate of ammonia,—a white precipitate.

R

Some of the water was boiled with a little nitric acid,—ammonia added to this gave no precipitate.

S

Oxalate of ammonia,—a precipitate.

T

nitrate of barytes,—a precipitate insoluble in nitric acid.

U

Nitrate of silver,—a white precipitate insoluble in nitric acid.

V

Sulphuretted hydrogen water,—no precipitate or change of colour; the water became very slightly turbid.

W

Prussiate of potash,—no immediate effect: after some weeks the water became slightly green.

X

Infusion of galls,—immediately a peach-blossom red colour, and very soon a precipitate which became dark purple by exposure to the air.

All the above effects are also produced after the water has been cooled, excepting that the colour of tincture of turmeric is not then destroyed, and, under some circumstances, no red colour occurs upon the addition of infusion of galls.

Y

A quantity of the water was evaporated to dryness, and distilled water added to the residuum. Nitrate of lime poured into the solution afforded a crystalline precipitate in a few hours, indicating the presence of an alkaline sulphate.

I shall now state the inferences to be deduced from these experiments.

Carbonic acid exists in this water (BE). A considerable portion of it escapes at the high temperature at which the water is obtained, its evolution occasioning precipitation of some substance which it held in solution (K).

From Experiment (L) it is evident that no sulphuretted hydrogen gas is present.

As no alteration of colour is effected upon tincture of litmus by the carbonic acid (M), it is evident that acid is present only in sufficient quantity to dissolve the substance precipitated by its evolution.

The destruction of the colour of tincture of turmeric (N) is clearly occasioned by the gas during its passage through the water (D).

The effect produced in experiment (O) is owing to the formation of carbonate of lime, and the precipitation of it and of the substance previously dissolved by carbonic acid (K).

A part of the precipitate obtained by adding ammonia (P) must have been similar to that of experiment (K), and to a portion of that of experiment (O), produced in (P) and (O) by combining the solvent carbonic acid instead of expelling it as in experiment (K). The precipitate was carbonate of lime, or of magnesia, or both.

As earthy carbonates are not precipitable by alkaline carbonates, the precipitate formed by carbonate of ammonia (Q) indicates the presence of some other earthy salt.

From experiment (R) it appears that no alumina or magnesia exists in the water, and that the precipitate obtained in experiment (K) was carbonate of lime. But according to Dr. Gibbes sulphate of alumina is present. It seems, however, that Dr. Saunders is perfectly correct in supposing that it forms no part of the saline contents of the water. In addition to the experiments already stated, it may be shewn to be incompatible with the salts actually existing in it; for the addition of a solution of sulphate of alumina occasions immediate precipitation.

As Dr. Gibbes has insisted on this point, I shall here mention what appear to have been the causes of his mistake. In reply to Dr. Saunders's supposition, that the precipitate which he took for alumina was carbonate of lime, he has stated that it was precipitated from the water by ammonia after oxalic acid had ceased to pro-

duce any further effect. This method is subject to error; for the oxalic acid appears to have been employed without previous combination with an alkali; and, as oxalate of lime is soluble in oxalic acid, it is evident that, if more of the latter were employed than was sufficient to precipitate the lime, it would dissolve a portion of oxalate of lime. The acid in combination with the lime previous to the addition of oxalic acid, not having an alkali to combine with, would dissolve a further portion of oxalate of lime; and unless the carbonic acid was expelled or saturated, it also would increase the error. From these circumstances I suspect that the precipitate afforded by ammonia was oxalate of lime, this compound being precipitable from acids by alkalies.

Experiment (S) determines the presence of lime.

Experiment (T) shows that sulphuric acid exists in the water.

The effect, produced by nitrate of silver (U) results from the action of muriatic acid.

As no metallic oxide, discoverable by fulphuretted hydrogen, was suspected, the appearance it produced (V) was supposed to be derived from its action upon carbonate of lime. This was ascertained to be the case by direct experiment.

The prussiate employed in experiment (W) was the triple compound containing oxide of iron. It was imagined that the slight greenness which was assumed by the water might be occasioned by the action of the carbonic acid, notwithstanding its holding carbonate of lime in solution, this effect being easily produced by the application of the stronger acids. A small quantity of the triple prussiate was therefore added to a solution of carbonate

of lime in carbonic acid: after a considerable time it acquired a green colour exactly similar to that observed in experiment (W). Dr. Falconer has indeed stated that a blue colour is to be obtained by the action of prussiate of potash upon the water; but, as it did not occur till after the addition of sulphuric acid, it is evident that this effect was produced by the action of the acid upon the oxide of iron of the prussiate.

Although the presence of oxide of iron is not at all indicated by prussiate of potash, (probably on account of the smallness of its quantity,) yet it is evident from the action of infusion of galls (X) that a minute portion of it actually exists in the water; the light colour of the recent precipitate, and its becoming darker by contact with atmospheric air, showing that it is in the state of protoxide. In making this experiment it is requisite to use a very small quantity of the infusion of galls; for, if much more than five drops of it are added to one ounce of the water, no indication of oxide of iron is produced, the water becoming of a light reddish brown colour, and affording no precipitate. An excess of this infusion reacts upon the compound of vegetable matter and oxide of iron so completely as to prevent the appearances readily presented by a small quantity.

From the well-known laws of chemical affinity it is evident that the oxide of iron is combined with carbonic acid; this compound undergoing some curious changes, which have occasioned much discussion.

It has been observed, that one of the most active tests of oxide of iron does not in this water produce any appearance of its presence; and the slight metallic taste which it communicates when hot and fresh has been un-

noticed by some analysts. This taste is lost by cooling, even in well-stopped bottles; and every method which I have tried to restore it has been unsuccessful. It has also been mentioned that the action of infusion of galls is in some cases lost.

The proofs that this water contains oxide of iron thus existing under singular circumstances, and liable to cease, it is not surprising that they have been assisted by collateral evidence. It has been asserted that the water deposits "a pale yellow ochrey precipitate;" but this is certainly an error, the precipitate being perfectly white. Another circumstance which has been adduced to prove the precipitation of oxide of iron is, that the sides of the king's bath become encrusted with it: this observation, as to fact, is correct; but the oxide appears not to be deposited from the water, but derived from the stone, by the increased oxidizement of the iron contained in it, by the alternate application of air and water. Having procured a specimen of oolite similar to that of which the sides of the bath are constructed, I added a drop or two of nitric acid to it; by this the iron became instantly and completely oxidized, affording an appearance similar to that which has been supposed to be deposited from the water.

Another fact has been noticed equally deceptive with the above stated, which is, that the clothes of the bathers become stained with iron moulds. It is indeed true, that the bright yellow colour of the substance of which these clothes are made changes to a brown; but this change is not partial, nor has it any resemblance to iron-moulds: it seems to be effected merely by the decay of the colouring matter, and I find that solutions of iron do not change the yellow colour.

The fact which has occasioned most discussion respecting the oxide of iron, is the loss of power of infusion of galls to detect it. The following experiments will show under what circumstances this occurs.

a

About one pint of the water was exposed, while hot, to the atmosphere in a vessel of broad surface. After it had remained about 16 hours, a small quantity of carbonate of lime was deposited by the evolution of carbonic acid gas. The precipitate was perfectly white, and had not the slightest appearance of containing oxide of iron. To this water infusion of galls was added without occasioning the least alteration of colour.

b

As the quantity of oxide of iron in the water is evidently extremely small, it may be imagined that it was precipitated with the carbonate of lime, but escaped observation from the minuteness of the quantity. To obviate this objection, some of the water was closely stopped in a vial for four or five days: upon examination it was found to possess its transparency perfectly, and without having afforded any precipitate; to some of this, infusion of galls was added without producing the slightest indication of oxide of iron.

c

Some of the water which had been cooled so as to retain its transparency, was heated to its original temperature; infusion of galls was then added, but without producing any effect.

The facts exhibited in experiments (*b*) and (*c*) have been long known, and have given rise to an idea that the iron is volatilized. Although this opinion is incompatible

with facts already mentioned, yet it may not be amiss to shew more particularly that it is completely erroneous. As it cannot be imagined that the temperature of the water is sufficient to volatilize mere oxide of iron, the existence of some substance capable of carrying it off must have been supposed. That muriatic acid and muriate of ammonia possess this power at high temperatures is well known, but no uncombined muriatic acid or muriate of ammonia is present. Hydrogen gas is said also to be capable of volatilizing iron; but the gas evolved from the water has been shown to consist of nitrogen gas and a small quantity of carbonic acid gas, and to neither of these gases, alone or combined, has any such power been attributed. If, however, they really possess it in this instance, they must be regarded as the solvent of the iron, and the effect produced upon infusion of galls must be derived from the gas diffused in small quantity through the water. If this be the case, the application of the concentrated solution of iron should produce a much more distinct effect upon the infusion; but it has been shown (D) that the gas destroys the colour of infusion of galls instead of increasing it, which would be the effect if it contained oxide of iron.

d

About one gallon of the water was put into a vessel of considerable depth, of which it occupied about two-thirds: it was slightly covered, and remained about twenty-four hours. It then retained its power of affording a peach-blossom coloured precipitate with infusion of galls (X) in a very considerable degree.

It is remarkable that in this experiment the result should have proved so different from that obtained in one

where the circumstances were similar, excepting only the form of the vessel and the quantity of the water. When the water was exposed with a broad surface, infusion of galls showed no action on it (*a*); but here, even after eight hours longer exposure, it detected oxide of iron.

From this circumstance I began to suspect that some change was produced by the absorption of oxygen, and that it had not produced the same effect in this as in the former experiment, on account of the quantity of the water and depth of the vessel. There appeared, however, a strong fact against this supposition; viz. that iron is more easily detected when highly oxidized, whereas the reverse effect in this case was produced.

To try the effect of atmospheric air, the following experiments were performed:

e

A small quantity of the water was enclosed, while hot, in a well-stopped vial, with about one-fortieth of its volume of atmospheric air. After four days the water remained perfectly transparent, but the addition of infusion of galls did not afford the slightest appearance of its containing iron.

f

Another portion of the water was kept for the same length of time in a well-stopped vial, but without any air except such as the water held in solution. Infusion of galls occasioned exactly the same appearance of iron in this as in the water when fresh and hot (X).

That the action of infusion of galls is lost by the absorption of the oxygen of atmospheric air is proved by the following experiment:

B

A third quantity of the water was enclosed, with the usual precaution, in a vial, about one half of which was occupied by the gas evolved from the water in the bath, which has been shewn to contain no oxygen gas. After four days, infusion of galls was added to it, and gave the same appearances of oxide of iron as occur in its application to the fresh hot water.

Having thus ascertained the effect of oxygen in preventing the action of infusion of galls upon oxide of iron, it remained to be shewn in what manner this is effected. I imagined it might be produced by increasing the power of combination of the oxide of iron so as to admit of its acting upon the earthy contents of the water and forming compounds, the strong affinity of the constituents of which prevented the action of the infusion of galls. With a view to ascertain how far this supposition was correct, I examined the effects produced by adding carbonate of lime, dissolved by carbonic acid, to solution of sulphate of iron to which infusion of galls had been previously added; and although it will appear, by the following experiments, that the alterations produced upon the oxide of iron in the water are caused by the carbonate of lime it contains, it will also be found that they are not effected in the way I had supposed.

A very dilute solution of green sulphate of iron was prepared: the quantity of oxide of iron contained in it was so small as scarcely to afford any alteration of colour when infusion of galls was added to it; but upon pouring solution of carbonate of lime into it after infusion of galls had been added, a deep red colour was almost instantaneously produced.

Although this fact did not immediately appear likely to solve the difficulties attendant upon the water in question, yet it was sufficiently striking to merit an examination by what means the carbonate of lime produced this effect, and to what extent it might be employed in rendering infusion of galls a more active re-agent.

With this intention I boiled some crystallized sulphate of iron in alcohol till nearly the whole of the red sulphate was separated. The remaining quantity being extremely small, I shall consider the iron in this solution as entirely in the state of protoxide. The sulphate, insoluble in alcohol, was dissolved in water, and the quantity of the oxide contained in a given portion of the solution was ascertained by taking the average of two experiments.

b

To one ounce of this solution, containing $\frac{1}{1000}$ dth of a grain of protoxide of iron, infusion of galls was added. This occasioned the usual appearances indicated by the presence of oxide of iron in a very slight degree. The colour produced, increased by the absorption of the oxygen of the atmosphere.

i

An equal quantity of the solution was treated with prussiate of potash. A light blue colour was immediately produced by the minute portion of peroxide of iron which had escaped the action of the alcohol: the intensity of this colour was gradually increased by the action of atmospheric air till the iron had arrived at its maximum of oxidizement.

k

Infusion of galls was added to one ounce of a dilute solution of carbonate of lime containing $\frac{1}{1000}$ dth of a

grain of oxide, as in the former experiments. A red purple colour, of very considerable intensity, was immediately produced.

l

The last experiment was repeated, employing only $\frac{1}{10000}$ dth of a grain of oxide, instead of $\frac{1}{1000}$ dth. A very distinct red purple was immediately produced by the action of the infusion of galls.

m

To one ounce of a solution of carbonate of lime, containing $\frac{1}{1000}$ dth of a grain of oxide, prussiate of potash was added; but it did not produce any indication of having acted upon the oxide of iron.

I now prepared a solution of red sulphate of iron by treating the green sulphate with nitric acid in a red heat. The quantity of oxide which the solution contained was as in the former case ascertained. The experiments made with this were as follow :

n

One ounce of a solution of red sulphate of iron, containing $\frac{1}{1000}$ dth of a grain of oxide, was treated with infusion of galls. The usual indications of its action upon oxide of iron were presented.

o

The addition of prussiate of potash to an equal quantity of the solution immediately occasioned a blue colour.

p

Infusion of galls was added to one ounce of a dilute solution of carbonate of lime containing $\frac{1}{1000}$ dth of a grain of the peroxide of iron. Slight indications of its action upon the oxide were produced, but the colour was scarcely more intense than that effected by $\frac{1}{10000}$ dth of a

grain of protoxide in similar circumstances: no effect whatever was produced by infusion of galls upon $\frac{1}{10000}$ th of a grain of peroxide in one ounce of solution of carbonate of lime. The colour produced when carbonate of lime and infusion of galls are added to the peroxide is red purple, similar to that occasioned by their action upon the protoxide.

9

To one ounce of a solution of carbonate of lime, containing, as in the last experiment, $\frac{1}{10000}$ th of a grain of peroxide of iron, prussiate of potash was added. Not the slightest blue colour was produced. When carbonate of lime was thus added to the solution of peroxide of iron, I found that it was capable of preventing the action of prussiate of potash upon $\frac{1}{250}$ th of a grain.

From these experiments it is evident that carbonate of lime possesses, in a very great degree, the power of increasing the action of infusion of galls upon protoxide of iron; while, on the contrary, it diminishes its power in detecting peroxide of iron; and is, moreover, capable of preventing the action of prussiate of potash.

The application of these experiments to the circumstances of the water in question is obvious. It has been shewn that it contains carbonate of lime; and that the power of infusion of galls to detect the oxide of iron it contains is completely lost by the absorption of oxygen. The following experiment was made with the intention of trying whether this effect of slow oxidizement might be imitated.

r

Infusion of galls is, as has been seen, capable of acting upon $\frac{1}{10000}$ th of a grain of protoxide of iron in

one ounce of solution of carbonate of lime (l). A portion of fulphate of iron containing $\frac{1}{5000}$ th of a grain of protoxide was dissolved in one ounce of dilute solution of carbonate of lime, and was kept in contact, with about one-fourth of its volume of atmospheric air, during twenty-four hours. At the end of that time the solution remained perfectly transparent, and without having precipitated; but the addition of infusion of galls did not occasion the slightest appearance of having acted upon the oxide of iron. In this experiment the loss of power of infusion of galls is much more speedily effected than in the Bath water. This is evidently owing to the atmospheric air contained in the distilled water employed, while no oxygen gas is present in the Bath water.

When carbonate of lime is added to fulphate of iron it is well known that double decomposition takes place, the iron being thus combined with the carbonic acid instead of the sulphuric. Having found that infusion of galls, in several instances, acts much more readily upon carbonates than fulphates, I imagined that the carbonate of lime produced its effect in this way. To ascertain whether this supposition was correct I made the following experiment :

A quantity of the solution of green fulphate of iron, similar to that employed in the above-related experiments, was decomposed by carbonate of potash; carbonic acid gas was passed through water in which the washed carbonate of iron was diffused, and to some of the filtered solution infusion of galls was added; but, instead of the red purple colour effected by the action of carbo-

nate of lime upon fulphate of iron and infusion of galls (k) and (l), the usual deep blue colour was obtained.

t

One tenth of the quantity of carbonate of iron employed in the last experiment was dissolved in a solution of carbonate of lime equal in measure to the last solution. To this infusion of galls was added. The red purple colour was immediately produced, and from its intensity it was evident that carbonate of lime had increased the power of infusion of galls as much in employing the carbonate as the fulphate of iron.

It may be concluded, from these experiments, that the effects produced by carbonate of lime are not attributable entirely, if at all, to the conversion of the fulphate of iron into a carbonate. Hence I was induced to examine the appearances produced by the action of the various alkalies and earths upon infusion of galls and solutions of iron. The results are by no means uninteresting, but the limits usually allotted to an analysis will hardly admit of the necessary details; I have therefore related only such facts as appeared requisite to explain the changes occurring in the Bath water, reserving the statement of the remaining experiments for a future opportunity.

I next examined the salts produced by evaporating the water and crystallization.

u

A quantity of the water was evaporated to dryness: the residuum was treated with distilled water as long as that fluid continued to dissolve any portion of it. This solution was again evaporated, and upon cooling yielded a considerable quantity of acicular crystals. These were again dissolved in distilled water; and to a part of

the solution nitrate of barytes was added, which occasioned a copious precipitate. The same effect was produced by oxalate of ammonia; but ammonia caused no precipitation. These crystals were therefore sulphate of lime. By further evaporation the solution afforded cubic crystals of muriate of soda and prismatic crystals of sulphate of soda.

The next object to be attained was the weight of the total quantity of the various substances held in solution by a given portion of the water. This has been given, with considerable variation, by different analysts, as will appear by the following statement. From a quart of the water

Dr. Lucas obtained $33\frac{1}{2}$ grains of dry residuum.

Dr. Charlton . 34

Dr. Falconer . $17\frac{3}{4}$

Dr. Gibbes . . $23\frac{1}{4}$

To account for the great difference of these results, Dr. Saunders has supposed that the water varies at different times, or that the residuum has been dried with various degrees of heat. I have ascertained the quantity of the contents of the water several times during about eighteen months, without observing any other variation in its weight than is unavoidable in experiment. In support of this observation it may be remarked, that I found its specific gravity exactly as stated by Dr. Falconer.

It is scarcely probable that the results of any of these analyses were obtained by drying the residuum at a lower temperature than 212° , or at a greater than a red heat. Now I find that one quart of the water, weighing 30 troy ounces 172 grains, at the temperature of 63° , gives 32 grains of residuum dried at 212° : when the heat of a sand-bath is employed, 30 grains are obtained; and at a

red heat, 28 grains. The greatest variation afforded by these methods is four grains; whereas from some cause, which it is difficult to explain, the extreme difference of the experiments above cited is $16\frac{1}{4}$ grains. When a red heat is employed, a part of the loss is occasioned by the decomposition of the carbonate of lime; for water poured upon the residuum turns turmeric paper of a reddish brown colour. The greater part of the residuum is perfectly white; the portion deposited at the upper part of the vessel is, however, slightly greyish, but not at all appearing as if coloured by oxide of iron. I suspected that it might be occasioned by carbonaceous matter: to ascertain whether this was the case, the following experiment was made:

20

Four pints of the water were evaporated to dryness in a retort; and the residuum boiled with about five ounces of alcohol. The filtered solution left, on evaporation, 8·3 grains of a yellowish-coloured substance. A part of this was dissolved in water, and afforded a copious white precipitate with nitrate of silver, but did not give any with ammonia or with carbonate of ammonia: muriate of soda was therefore the only salt dissolved by the alcohol.

20

To the remaining portion of the saline mass colourless sulphuric acid was added. By heating, the acid acquired a dark brown colour, evidently derived from its action upon carbonaceous matter. This experiment did not appear conclusive, as two causes of error might have existed,—a small quantity of alcohol was probably decomposed by the action of the salts upon it, or some of

the conferva which is found in the water might have escaped notice previous to evaporation. I had recourse, therefore, to other means. Mr. Kirwan, in his Treatise on the Analysis of Mineral Waters, gives a method for ascertaining the presence and quantity of extractive matter proposed by Westrumb, which consists in precipitating the muriatic salts by nitrate of lead, and afterwards the extractive matter by nitrate of silver. It is impossible to conceive any method more completely fallacious than this; for extractive matter is as readily precipitated by nitrate of lead as by nitrate of silver; and although muriate of soda is decomposed by nitrate of lead, muriate of lead being a salt of considerable solubility, the subsequent addition of nitrate of silver would decompose it, and afford a precipitate consisting of muriate of silver without any extractive matter.

The power of sulphuric acid to detect carbonaceous matter is extremely great: $\frac{1}{1000}$ th of a grain of sugar was dissolved in four ounces of water; to this solution about one ounce of sulphuric acid was added; it was then boiled till nearly the whole of the water was evaporated, and the acid had acquired a very distinct brown colour.

The following experiment was now made;

~

A quantity of sulphuric acid was added to one quart of the water perfectly transparent, and free from heterogeneous matter. The mixture was evaporated nearly to dryness in a retort, and the acid remained perfectly colourless. The water, therefore, contains no carbonaceous matter.

The substances contained in the water, as shown by the foregoing experiments, are; carbonate of lime,

oxide of iron, sulphate of lime, muriate of soda, and sulphate of soda. The presence of these compounds has been universally allowed; but that silica is contained in the water, was discovered by Dr. Gibbes. To find the quantity of each of these, the following methods were employed:

y

A quart of the water was evaporated to dryness in a platina crucible: the residuum, dried in a sand heat, weighed thirty grains. This was boiled, with successive portions of distilled water, till it ceased to afford a precipitate with nitrate of barytes. The solution was then divided into three equal quantities.

z

To one of these portions nitrate of silver was added as long as precipitation took place, and distilled water was poured upon the precipitate till it came away quite pure. The muriate of silver thus obtained was weighed after exsiccation.

A

The second quantity was treated with oxalate of ammonia while it continued to produce any effect. The precipitated oxalate of lime was washed, dried, and weighed.

B

To the remaining part of the solution nitrate of barytes was added till it ceased to produce any precipitate; and the sulphate of barytes obtained by its action was weighed, after washing and drying, as in the former experiments.

C

The residuum, insoluble in water, weighed, when dried, two grains: nitric acid added to it dissolved 1·7

grains. This solution afforded no precipitate with ammonia, but a copious one with oxalate of ammonia: it was therefore nitrate of lime obtained by the decomposition of the carbonate.

D

The $\frac{1}{3}$ of a grain left by the nitric acid was dissolved by potash, and precipitated from it by muriate of ammonia. This precipitate was not again soluble in nitric acid, and was consequently silica.

Another quart of the water was treated in the same way. To avoid prolixity, I shall state the quantity of each precipitate afforded by one-third of a quart multiplied by three, and make the requisite calculations from the mean of the two experiments.

	Exp. I.	Exp. II.	Mean.
Residuum . . .	30	30	30 grain
Muriate of silver .	16.2	16.2	16.2 do.
Oxalate of lime .	18.3	17.7	18 do.
Sulphate of barytes	36.6	36.9	36.7 do.
Carbonate of lime	1.7	1.5	1.6 do.
Silica3	.4	.35 do.

According to Dr. Gibbes, a quart of the water affords nearly 4 grains of silica when treated in the method I have described. Thinking it probable that a portion of it might be taken up by the action of the salts during their solution in water, I tried whether any larger quantity could be obtained by the following method:

E

A quart of the water was evaporated to dryness in a platina crucible. The residuum was repeatedly treated with nitric acid in a red heat; the soluble parts were again dissolved by distilled water, and the portion info-

luble in it, when dried, weighed $\cdot 4$ of a grain. This agreeing exactly with the last experiment, I shall consider as the quantity of filica afforded by a quart of the water. This experiment was several times repeated, with very little variation in the weight of the result, but was sometimes evidently coloured by oxide of iron, which was separated from the filica, and its nature ascertained by the usual means. But, even when employing apparently perfectly similar means, the oxide of iron was not always to be obtained,—an effect attributable to the decomposition of the muriate of soda by the nitric acid, and to the power which muriatic acid possesses of carrying off oxide of iron; but for the uncertainty of its action it is not easy to account.

To find the quantity of oxide of iron contained in the water, the following means were employed:

F

To a quantity of the hot water infusion of galls was added in the requisite proportion. The water measured when cold $9\frac{1}{2}$ pints. The precipitate obtained was separated by the filter, and dried:—the precipitate and filter were then burned together in a platina crucible, and the carbonaceous matter of the filter, and that combined with the iron, were got rid of by the application of a red heat. The residuum was then treated with nitric acid, in order completely to oxidize the iron:—it was then boiled with acetic acid to take up the lime precipitated with the oxide of iron by the infusion of galls; and afterwards with potash, to dissolve any filica which the filter might have furnished—the remaining substance was evidently oxide of iron, and weighed $\cdot 2$ of a grain.

G

The last experiment was repeated, slightly varying the method. Infusion of galls was added, as before, to a quantity of the hot water, measuring after it had cooled $17\frac{1}{4}$ pints. The precipitate was suffered to subside, and the water poured off till only a small quantity remained. This was evaporated, and the residuum, treated with nitric acid in a red heat, weighed $\cdot 5$ of a grain. Being exposed to a red heat with carbonaceous matter, it became magnetic, and dissolved in muriatic acid, except $\frac{1}{16}$ th of a grain, which appeared to be silica, derived from the water evaporated to obtain the precipitate formed by infusion of galls. The muriatic solution afforded a blue precipitate with prussiate of potash, $\cdot 4$ were therefore oxide of iron.

According to the experiment (*F*) one quart of the water affords $\cdot 00421$ of a grain of oxide of iron, and by the second $\cdot 00463$, giving a mean of $\cdot 00442$; but the iron in the water is in the state of protoxide; and as the peroxide consists of $66\cdot 5$ protoxide, and $33\cdot 5$ oxygen, $\cdot 00442$ will give $\cdot 00394$, the quantity of protoxide of iron in one quart.

242 of muriate of silver indicate 100 of muriate of soda, 16 \cdot 2 will therefore give 6 \cdot 6.

100 of oxalate of lime are produced by 100 of sulphate of lime, 18 will then give 18.

100 of sulphate of lime afford 175 of sulphate of barytes, 18 will then produce 31 \cdot 5, which subtracted from 36 \cdot 7, the whole quantity of sulphate of barytes obtained, leave 5 \cdot 2 for the sulphate of barytes formed by the sulphate of soda; and as 100 of sulphate of soda give 170 of sulphate of barytes, 5 \cdot 2 yield 3.

One quart of the water therefore contains

Carbonic acid	.	2.4	inches.
Sulphate of lime	.	18.	grains.
Muriate of soda	.	6.6	
Sulphate of soda	.	3.0	
Carbonate of lime	.	1.6	
Silica	.	.4	
Oxide of iron	.	.00394	
		<hr/>	
		29.60394	
Loss	.	.39606	
		<hr/>	
		30.	
		<hr/>	

Estimating the muriate and sulphate of soda in the crystallized state, one pint of the water contains nearly as follows :

Carbonic acid	.	1 $\frac{1}{2}$	inch.
Sulphate of lime	.	9	grains.
Muriate of soda	.	3 $\frac{1}{2}$	
Sulphate of soda	.	3 $\frac{1}{2}$	
Carbonate of lime	.	$\frac{8}{16}$	
Silica	.	$\frac{1}{5}$	
Oxide of iron	.	$\frac{1}{64}$	

FINIS.

